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*Publication date:*
2016

*Document Version*
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

*Citation (APA):*
Engelbrekt, C., Law, M., & Zhang, J. (2016). *Composite nanomaterials of semiconductors and noble metals as plasmonic photocatalysts*. Poster session presented at International Conference on Advances in Semiconductors and Catalysts for Photoelectrochemical Fuel Production (SolarFuel16), Berlin, Germany.

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# Composite nanomaterials of semiconductors and noble metals as plasmonic photocatalysts

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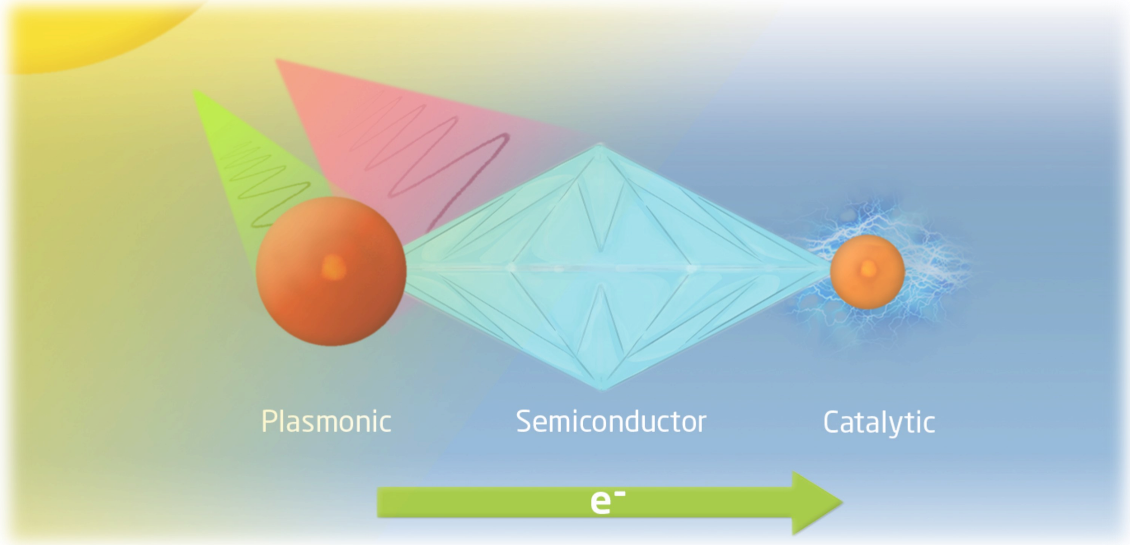
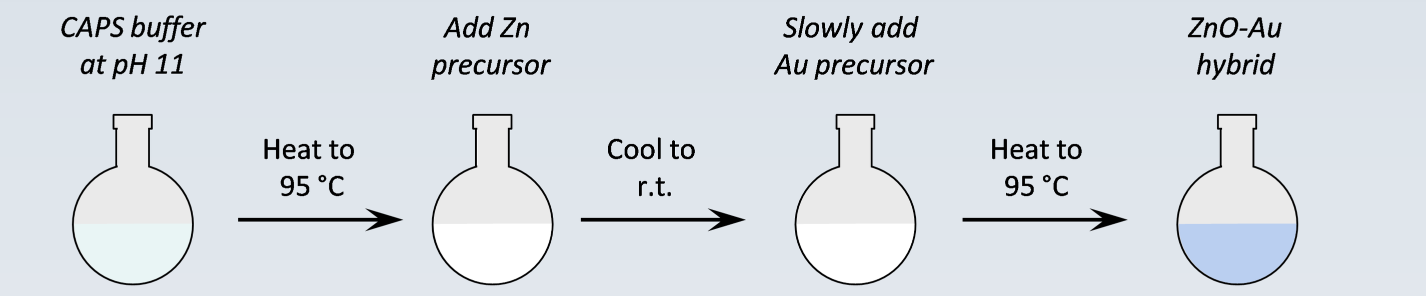
Harnessing sunlight and storing the energy in chemical bonds is an important element in the transition towards green and sustainable technologies. Solar fuel production requires photocatalysts that (1) absorb large parts of the solar spectrum, (2) generate charges with significant lifetimes and appropriate energies, (3) catalyze relevant chemical transformations from abundant, low-energy starting materials, and (4) are stable under operating conditions. A new avenue within solar fuels involve plasmonic metal nanoparticles (PNPs). These materials have tunable optical properties, exciting catalytic behavior, and can be more stable under operating conditions. Composite photocatalysts of semiconductor nanoparticles (SNPs) and PNPs exploit broadly the solar spectrum, provide new catalytic routes and expand the scope of solar photocatalysis.

The newly initiated project aims at developing composite nanomaterials of SNPs and PNPs from mild, aqueous synthesis protocols and testing the catalytic properties of these plasmonic photocatalysts.




## ONE-POT SYNTHESIS AND CHARACTERIZATION OF ZnO-AuNP HYBRID




*Scheme 1. Synthesis of ZnO and ZnO-Au hybrids. N-cyclohexyl-3-aminopropane-sulfonic acid (CAPS) buffer is adjusted to pH 11 and heated to 95 °C before addition of Zn precursor solution. After formation of ZnO, the mixture is cooled and $HAuCl_4$ is added dropwise. Finally, the mixture is heated again reducing the Au precursor forming ZnO hybrids.*

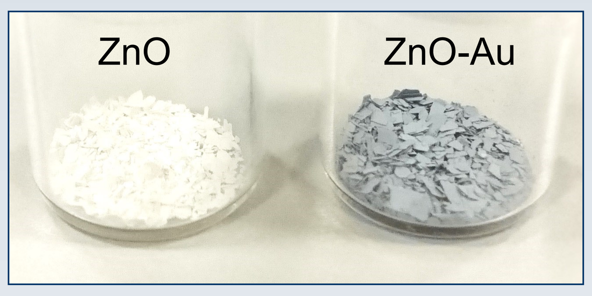



*Figure 1. Purified and dried nanopowder of pure ZnO (left) or ZnO-AuNP hybrid nanomaterial (right). The low loading of Au results in a drastic colour change.*

Composite nanomaterials of ZnO nanobipyramids tipped with anisotropic AuNPs were prepared under mild conditions in buffered aqueous solution in one pot by sequential precipitation of ZnO from $Zn(OAc)_2$ and deposition of gold by reduction of $HAuCl_4$. In both steps, the CAPS buffer plays a central role. During ZnO formation, the buffer ensures stable alkaline conditions preventing pH from dropping as the oxide is formed. It potentially adsorbs on the ZnO surface contributing to shape control. In the second step, AuNP formation, CAPS acts as the reducing agent while getting oxidized to form amine oxide.

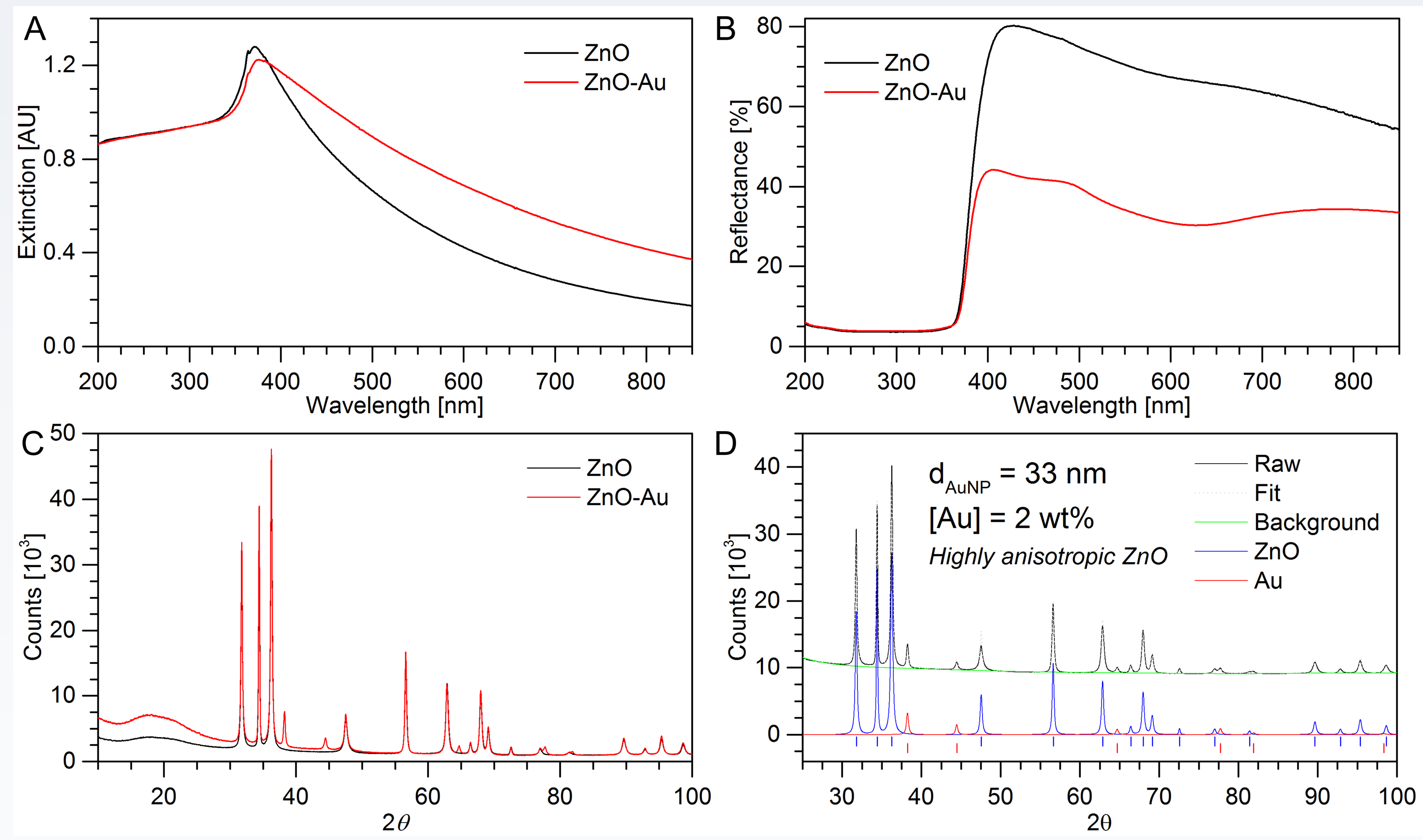
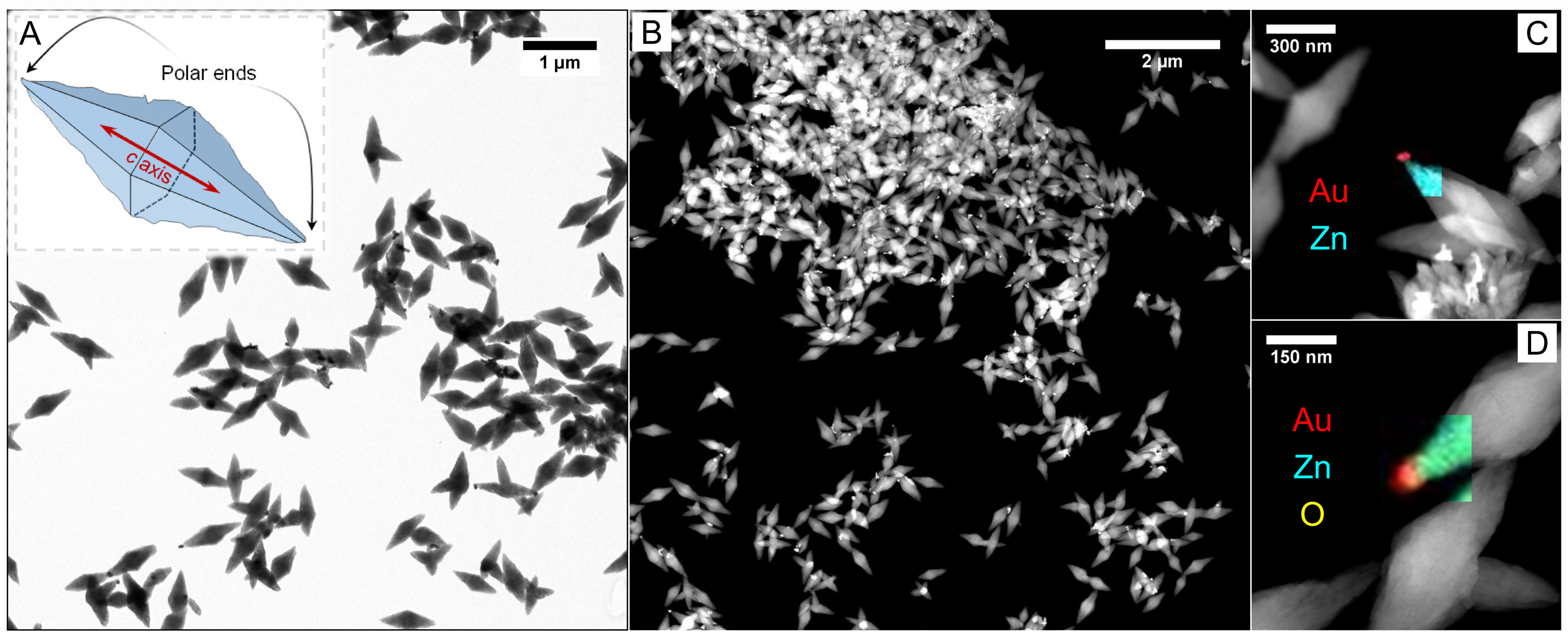


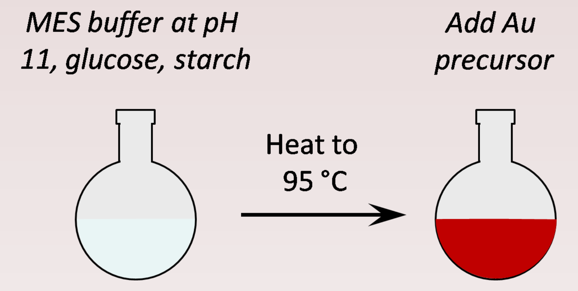

*Figure 2. (A) Extinction spectra of purified and redispersed nanostructures in solution. (B) Reflectance spectrum of drop cast films on glass. (C) X-ray powder diffraction (XRD) patterns of obtained powders. (D) Rietveld refinement of XRD patterns confirming a low Au loading of a few wt% and highly anisotropic ZnO.*

The ZnO nanoparticles have a measured band gap of 3.28 eV, as expected, and broad scattering in the visible. The addition of small (2 wt%) amounts of gold increased significantly the absorbance in the visible with a broad feature around 600 nm resulting in a colour change from white to purple. Transmission electron microscopy (TEM), scanning TEM (STEM) and elemental mapping by energy dispersive X-ray spectroscopy (STEM-EDS) reveals that ZnO grows to form 900 ± 200 nm "nanobipyramids" and upon reduction of the Au precursor, anisotropic AuNPs of 20-50 nm are deposited on the ZnO surfaces. The base and tips of the nanobipyramids are made up of the polar <001> facets which may be a responsible for the slightly selective deposition of gold at the tips.

*Figure 3. (A) TEM and (B) STEM images of ZnO-Au hybrids. (C-D) STEM-EDS elemental maps of individual nano-particles showing Au tips on ZnO nanobipyramids. Inset in (A) shows a model of the ZnO nanobipyramids .*



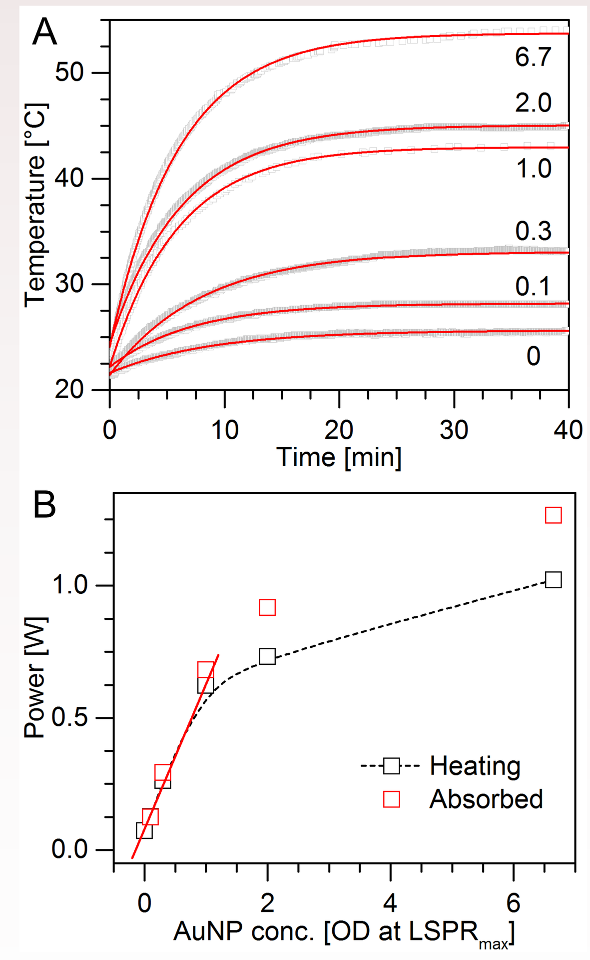

## AuNPs AND PLASMONIC HEATING




*Scheme 2. AuNPs were synthesized according to the SAMENS method. $HAuCl_4$ is reduced by 2-(N-morpholino) ethane-sulfonic acid (MES) and stabilized by starch at neutral pH.*

Plasmonic heating is a strong effect and will be convoluted by other photocatalytic effects during solar fuel generation. Initial experiments show how upon illumination with white light, AuNPs increase the bulk temperature of the solution by around 10 W/$g_{Au}$.

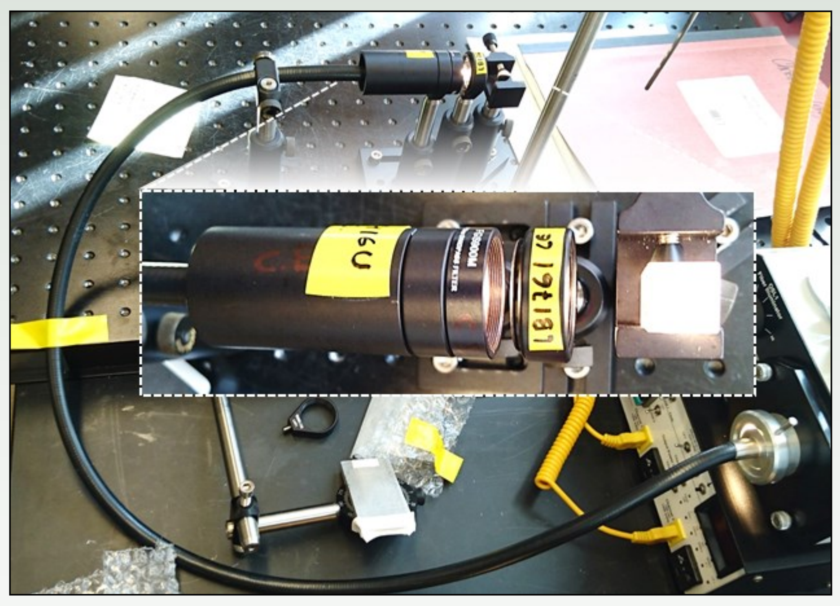
*Figure 4→. (A) Temperature change during white light illumination at different concentrations (optical density, OD). (B) Estimated heating power as function of AuNP concentration.*





*←Figure 5. Pasmonic heating setup. The tungsten -halogen light is filtered (passing 315-710 nm), and focused onto the cuvette and temperature monitored above the illuminated area.*

## NEXT STEP: PHOTOCATALYSIS



The setup shown above has been established and will be used for assessing the photocatalytic properties of the single component and hybrid nanomaterials. The fiber bundle tip is mounted in a collimating tube making the setup very flexible for use with other instrumentation. The estimated power output of the IR filtered beam is 300 mW.

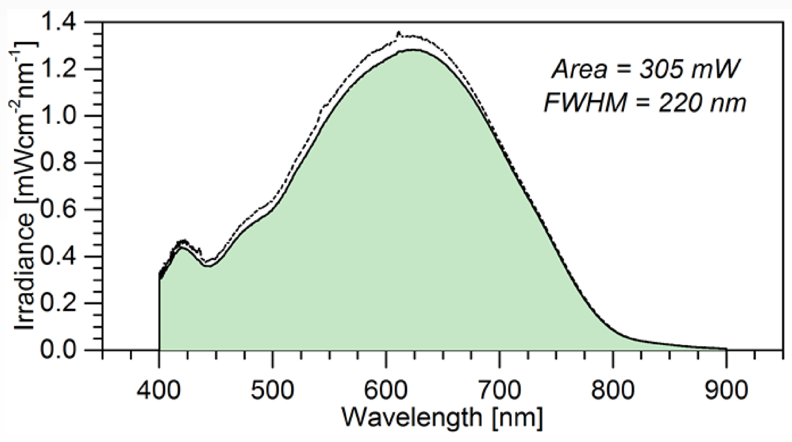



*Figure 6. Spectral irradiance of the focused, infrared-filtered beam*

## CONCLUSIONS and OUTLOOK

The results presented here mark the very beginning of this project. Initial SNP/PNP hybrids of ZnO *and* Au were prepared demonstrating the buffered one-pot approach. More uniform products will be the target of further optimization of the synthesis. The geometry of the hybrid may provide good separation of oxidation and reduction sites while charge conduction along the c axis provides charge separation. Apolar facets of ZnO are generally less active for photocatalysis but this might be overcome by the rough/ stepped surface of the nanobipyramids. This, and the influence of gold, will be probed using the described light delivery system coupled with other techniques such as GC-MS and electrochemistry for product analysis.

## ACKNOWLEDGENENT

Financial support from the Danish Council for Independent Research for the project *Development of new metal oxide/noble metal hybrids as plasmonic bifunctional nanocatalysts for solar energy* (DFF 5054-00107) is acknowledged.